Derivative Chronopotentiometry of Multicomponent Systems

(Abstract)

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In a previous paper[1], derivative chronopotentiometry was applied to systems of only one electroactive species. In this paper the method is extended to systems with several electroactive species.

Using the Response Function Additivity Principle of Murray and Reilley[2], the bulk concentration of the j-th component is given by equation (1).

$$C_{o,j}^{*} = \frac{2i_o}{n_j F (\pi D_{o,j})^{1/2}} \left[\left(\sum_{m=1}^{j} \tau_m \right)^{1/2} - \left(\sum_{m=1}^{j-1} \tau_m \right)^{1/2} \right] \tag{1}$$

During the j-th step of the chronopotentiogram $\left(\sum_{m=1}^{j} \tau_m > t > \sum_{m=1}^{j-1} \tau_m \right)$

$$D_{o,j}^{1/2} [C_{o,j}^{*} - C_{o,j(o,t)}] = D_{r,j}^{1/2} C_{r,j(o,t)} = \frac{2i_o}{n_j F \pi^{1/2}} \left[t^{1/2} - \left(\sum_{m=1}^{j-1} \tau_m \right)^{1/2} \right] \tag{2}$$

Solving equations (1) and (2) for $C_{o,j(o,t)}$ and $C_{r,j(o,t)}$

$$C_{o,j(o,t)} = \frac{2i_o}{n_j F (\pi D_{o,j})^{1/2}} \left[\left(\sum_{m=1}^{j} \tau_m \right)^{1/2} - t^{1/2} \right] \tag{3}$$

$$C_{r,j(o,t)} = \frac{2i_o}{n_j F (\pi D_{r,j})^{1/2}} \left[t^{1/2} - \left(\sum_{m=1}^{j-1} \tau_m \right)^{1/2} \right] \tag{4}$$

If the j-th component is reversible, the potential time relationship is obtained by substituting equations (3) and (4) into the Nernst equation.

$$E = E_{1/2} + \frac{RT}{n_j F} \text{Ln} \frac{\left[\left(\sum_{m=1}^{j} \tau_m \right)^{1/2} - t^{1/2} \right]}{\left[t^{1/2} - \left(\sum_{m=1}^{j-1} \tau_m \right)^{1/2} \right]} \tag{5}$$

Differentiating equation (5)

$$\frac{dE}{dt} = \frac{-RT}{2n_j F\, t^{1/2}} \left[\frac{1}{\left(\sum\limits_{m=1}^{j} \tau_m\right)^{1/2} - t^{1/2}} + \frac{1}{t^{1/2} - \left(\sum\limits_{m=1}^{j-1} \tau_m\right)^{1/2}} \right] \quad (6)$$

For the case, $j=1$, equations (5) and (6) reduce to those for a single component system[3]. The minimum of the derivative function is evaluated by taking the second derivative and equating it to zero.

$$n_j \left(\sum\limits_{m=1}^{j-1} \tau_m\right)\left(\frac{dE}{dt}\right)_{min} = \frac{-4.5\ RT/F}{a+1 + (a^2-a+1)^{1/2}} \left[\frac{1}{2a-1-(a^2-a+1)^{1/2}} + \right.$$

$$\left. \frac{1}{a+(a^2-a+1)^{1/2}-2} \right] \quad (7)$$

where

$$a = \frac{\left(\sum\limits_{m=1}^{j} \tau_m\right)^{1/2}}{\left(\sum\limits_{m=1}^{j-1} \tau_m\right)^{1/2}} = \frac{\sum\limits_{m=1}^{j} n_m C_{o,m}^{*} D_{o,m}^{1/2}}{\sum\limits_{m=1}^{j-1} n_m C_{o,m}^{*} D_{o,m}^{1/2}} \simeq \frac{\sum\limits_{m=1}^{j} n_m C_{o,m}^{*}}{\sum\limits_{m=1}^{j-1} n_m C_{o,m}^{*}} \quad (8)$$

A digital computer was programmed to solve the right side of equation (7) for specified values of "a" and to print out the results in tabular form. All of the terms on the left side of equation (7) are known or obtainable by experiment. Then the corresponding value of "a" can be read from the table.

Combining equations (1) and (8),

$$C_{o,j}^{*} = \frac{2i_o\ (a-1)}{n_j F(\pi D_{o,j})^{1/2}} \left(\sum\limits_{m=1}^{j-1} \tau_m\right)^{1/2} \quad (9)$$

Equation (9) may be used to obtain $C_{o,j}^{*}$ directly, provided the current density and diffusion coefficient $D_{o,j}$ are known with sufficient accuracy. If such is not the case, graphical, standard-addition techniques can be employed.

These standard-addition techniques are based on the fact that a plot of

$$C_{o,j}^{*} \quad \text{versus} \quad (a-1) \left(\sum_{m=1}^{j-1} \tau_m \right)^{1/2}$$

is a straight line through the origin. Thus such a plot can be constructed with $C_{o,j}^{*}$ added, and then the plot can be shifted along the concentration axis until the extrapolated line intersects the origin. The concentration, of the point for zero addition, then can be read off of the plot.

This procedure may be simplified if the addition is carried out without dilution of the species more reducible than the j-th species. For example, the sample may be split into two equal portions, the addition made to one portion and then both solutions diluted to the same total volume. Derivative chronopotentiograms are then performed on various mixtures of the two solutions. In this way $\sum_{m=1}^{j-1} \tau_m$ is kept constant and a plot of $C_{o,j}^{*}$ versus (a-1) is linear.

The preceding derivations do not consider the effect of the double-layer charging current. For single component systems, derivative chronopotentiometry is relatively insensitive to double-layer charging[3] and semiempirical correction techniques have proved effective[1]. However, the situation appears to be more serious for multicomponent systems. Work is continuing in these laboratories in an attempt to devise a correction technique similar to that devised for single component systems. An alternative approach is available, however, since an instrumental method for charging current correction has recently been reported[4].

References

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